

Title	Nuclear Magnetic Spin-Rotational Relaxation Times for Linear Molecules
Creators	McConnell, James
Date	1981
Citation	McConnell, James (1981) Nuclear Magnetic Spin-Rotational Relaxation Times for Linear Molecules. (Preprint)
URL	<a href="https://dair.dias.ie/id/eprint/947/">https://dair.dias.ie/id/eprint/947/</a>
DOI	DIAS-STP-81-24

81-24

NUCLEAR MAGNETIC SPIN-ROTATION  
RELAXATION TIMES FOR LINEAR MOLECULES

James McConnell

Dublin Institute for Advanced Studies  
Dublin 4, Ireland

---

The stochastic differential equation study of nuclear magnetic relaxation by spin-rotational interactions is applied to the linear rotator model of the molecule. Inertial effects are included in the calculations, which are performed analytically. Expressions are derived for the spin-rotational contributions to the longitudinal and transverse relaxation times, and for the spin-rotational correlation time.

---

1. INTRODUCTION

The general method for the calculation of relaxation times arising from nuclear magnetic spin-rotational interactions<sup>1)</sup> has been applied to both spherical<sup>1)</sup> and symmetric rotator molecules<sup>2)</sup>, that are subject to rotational thermal motion. The case of the linear molecule is now examined in detail. As a preparation, the rotation operator is expressed in a form that is convenient for carrying out the integrations that arise in the above method. When this has been done, expressions for relaxation times are calculated to a high degree of accuracy. The results are compared with those obtained for the spherical and the symmetric rotator models.

## 2. THE ROTATION OPERATOR

We consider the case of a rotating symmetric molecule which is so thin that it may be approximated by a needle-like rotator. It has zero component of angular velocity about its axis. We take rotating cartesian coordinate axes with origin at the centre of the needle, the third axis being along the line of symmetry and the other two axes perpendicular to this line and to one another. Denoting by  $\omega_1, \omega_2$  the components of angular velocity about the first and second axes, respectively, and by  $I$  the moment of inertia about these axes we write

$$\begin{aligned} I \dot{\omega}_1(t) &= -I B \omega_1(t) + I \frac{dW_1(t)}{dt} \\ I \dot{\omega}_2(t) &= -I B \omega_2(t) + I \frac{dW_2(t)}{dt} \end{aligned} \quad (1)$$

where  $B$  is a frictional constant and  $W_1(t), W_2(t)$  are Wiener processes. Equations (1) are linear and their steady state solutions are centred Gaussian random variables obeying

$$\langle \omega_1(t) \omega_2(t_m) \rangle = \delta_{ip} \frac{kT}{I} e^{-B|t-t_m|}, \quad (i, p = 1, 2) \quad (2)$$

where the angular brackets denote ensemble averages for the steady state,  $k$  is the Boltzmann constant and  $T$  the absolute temperature.

A method of investigating spin-rotational interactions has been set out in section 2 of ref. 1. The rotation operator  $R(t)$  that brings the molecular coordinate system at time zero to its orientation at a later time  $t$  satisfies the differential equation

$$\frac{dR(t)}{dt} = -i \left( \underline{J} \cdot \underline{\omega}(t) \right) R(t),$$

where the components  $J_1, J_2, J_3$  of  $\underline{J}$  satisfy the commutation relation

$$[J_\mu, J_\nu] = -i \left( \underline{J} \cdot \underline{e}_\mu \times \underline{e}_\nu \right) \quad (3)$$

and we interpret the scalar product  $(\underline{J} \cdot \underline{\omega}(t))$  as  $J_1 \omega_1(t) + J_2 \omega_2(t)$ . This restriction of the scalar product to the sum of two terms gives rise to complications that are not present in calculations for a spherical molecule.

The rotation operator obeys the equation <sup>3)</sup>

$$R(t) = \left( \underline{I} + \varepsilon^1 F^{(1)}(t) + \varepsilon^2 F^{(2)}(t) + \varepsilon^3 F^{(3)}(t) + \varepsilon^4 F^{(4)}(t) + \dots \right) \langle R(t) \rangle \quad (4)$$

where  $\underline{I}$  is the identity operator,  $\varepsilon^i F^{(i)}(t)$  are given by eq. (2.35), (2.36) of ref. 1 and  $\langle R(t) \rangle$  obeys <sup>4)</sup>

$$\frac{d\langle R(t) \rangle}{dt} = \left( \varepsilon^3 \mathcal{Q}^{(3)}(t) + \varepsilon^4 \mathcal{Q}^{(4)}(t) + \varepsilon^5 \mathcal{Q}^{(5)}(t) + \dots \right) \langle R(t) \rangle. \quad (5)$$

In this equation  $\varepsilon^{2n+1} \mathcal{Q}^{(2n+1)}(t)$  does not appear because it is the sum of products of averages of an odd number of  $\omega_j$ 's. The values of the  $\varepsilon^{1,2,3} \mathcal{Q}^{(1,2,3)}(t)$  in (5) are given by <sup>5)</sup>

$$\varepsilon^2 \mathcal{L}^{(2)}(t) = -\frac{kT}{I} (J^2 - J_3^2) \int_0^{t_1} e^{-B(t-t_2)} dt_2$$

$$= -\frac{kT}{I} (J^2 - J_3^2) \frac{dI^{(2)}(t)}{dt_1}$$

$$\varepsilon^4 \mathcal{L}^{(4)}(t) = -\left(\frac{kT}{I}\right)^2 (2J^2 - 5J_3^2) \int_0^{t_1} dt_2 \int_0^{t_2} dt_3 \int_0^{t_3} dt_4 e^{-B(t+t_2-t_3-t_4)}$$

$$= -\left(\frac{kT}{I}\right)^2 (2J^2 - 5J_3^2) \frac{dI_2^{(4)}(t)}{dt_1} \quad (6)$$

$$\begin{aligned} \varepsilon^6 \mathcal{L}^{(6)}(t) &= -\left(\frac{kT}{I}\right)^3 \left\{ [9(J^2 - J_3^2)J_3^2 + 4J^2 - 16J_3^2] \int_0^{t_1} dt_2 \int_0^{t_2} dt_3 \int_0^{t_3} dt_4 e^{-B(t+t_2-t_3-t_4-t_5-t_6)} \right. \\ &\quad \left. + [21(J^2 - J_3^2)J_3^2 + 20J^2 - 68J_3^2] \int_0^{t_1} dt_2 \int_0^{t_2} dt_3 \int_0^{t_3} dt_4 \int_0^{t_4} dt_5 e^{-B(t+t_2+t_3-t_4-t_5-t_6)} \right\} \\ &= -\left(\frac{kT}{I}\right)^3 \left\{ [9(J^2 - J_3^2)J_3^2 + 4J^2 - 16J_3^2] \frac{dI_3^{(6)}(t)}{dt_1} \right. \\ &\quad \left. + [21(J^2 - J_3^2)J_3^2 + 20J^2 - 68J_3^2] \frac{dI_4^{(6)}(t)}{dt_1} \right\}, \end{aligned}$$

where<sup>6)</sup>

$$I^{(1)}(t) = B^{-1} (Bt - 1 + e^{-Bt})$$

$$I_2^{(4)}(t) = B^{-4} \left\{ \frac{1}{2} Bt - \frac{5}{4} + [Bt + 1] e^{-Bt} + \frac{1}{4} e^{-2Bt} \right\}$$

$$I_3^{(6)}(t) = B^{-6} \left\{ \frac{1}{4} Bt - 1 + \left[ \frac{1}{2} B^2 t^2 + 2 \right] e^{-Bt} + \left[ \frac{1}{4} Bt + 1 \right] e^{-2Bt} \right\} \quad (7)$$

$$I_4^{(6)}(t) = B^{-6} \left\{ \frac{1}{12} Bt - \frac{5}{18} + \left[ \frac{1}{2} Bt - \frac{1}{4} \right] e^{-Bt} + \left[ \frac{1}{4} Bt + \frac{1}{2} \right] e^{-2Bt} + \frac{1}{36} e^{-3Bt} \right\}$$

and

$$J^2 = J_1^2 + J_2^2 + J_3^2$$

We define  $G$  by

$$G = \varepsilon^2 G^{(2)} + \varepsilon^4 G^{(4)} + \varepsilon^6 G^{(6)} + \dots$$

$$G^{(2n)} = \mathcal{L}^{(2n)}.$$

In the present problem

$$\varepsilon^2 G^{(2)} = -\gamma (J^2 - J_3^2) B, \quad \varepsilon^4 G^{(4)} = -\gamma^2 \left( J^2 - \frac{5}{2} J_3^2 \right) B$$

$$\varepsilon^6 G^{(6)} = -\gamma^3 \left[ 4(J^2 - J_3^2) J_3^2 + \frac{8}{3} J^2 - \frac{29}{3} J_3^2 \right] B$$

with

$$\gamma = \frac{kT}{IB^2}, \quad (8)$$

a small dimensionless constant. It follows that

$$G = -\gamma B \left\{ (J^2 - J_3^2) + \gamma \left( J^2 - \frac{5}{2} J_3^2 \right) + \gamma^2 \left[ \frac{8}{3} J^2 - \frac{29}{3} J_3^2 + 4(J^2 - J_3^2) J_3^2 \right] + \dots \right\}. \quad (9)$$

In order to express  $\langle R(t) \rangle$  in a form that is useful for further computation we employ the Krylov-Bogoliubov method<sup>7)</sup>. This means that we must put<sup>8)</sup>

$$\langle R(t) \rangle = \left( \mathbb{I} + \varepsilon^2 V^{(2)}(t) + \varepsilon^4 V^{(4)}(t) + \dots \right) e^{Gt}, \quad (10)$$

where  $V^{(2)}(t)$  and  $V^{(4)}(t)$  satisfy

$$\frac{dV^{(2)}(t)}{dt} = \Omega^{(2)}(t) - G^{(2)} \\ \frac{dV^{(4)}(t)}{dt} = \Omega^{(4)}(t) - G^{(4)} + (\Omega^{(2)}(t) - G^{(2)})V^{(2)}(t).$$

On integrating these equations we obtain

$$\varepsilon^2 V^{(2)}(t) = \gamma(J^2 - J_3^2)(1 - e^{-\beta t}) \\ \varepsilon^4 V^{(4)}(t) = \gamma^2 \left\{ (2J^2 - 5J_3^2) \left( \frac{\beta}{4} - \beta t e^{-\beta t} - e^{-\beta t} - \frac{1}{4} e^{-2\beta t} \right) \right. \\ \left. + (J^2 - J_3^2)^2 \left( \frac{1}{2} - e^{-\beta t} + \frac{1}{2} e^{-2\beta t} \right) \right\}$$

and hence, from (9) and (10),

$$\langle R(t) \rangle = \left\{ \frac{1}{2} + \gamma(J^2 - J_3^2)(1 - e^{-\beta t}) + \gamma^2 \left[ (2J^2 - 5J_3^2) \left( \frac{\beta}{4} - \beta t e^{-\beta t} - e^{-\beta t} - \frac{1}{4} e^{-2\beta t} \right) \right. \right. \\ \left. \left. + (J^2 - J_3^2)^2 \left( \frac{1}{2} - e^{-\beta t} + \frac{1}{2} e^{-2\beta t} \right) \right] + \dots \right\} \\ \times \exp \left[ -\gamma B \left\{ (J^2 - J_3^2) + \gamma(J^2 - \frac{5}{2} J_3^2) \right. \right. \\ \left. \left. + \gamma^2 \left( \frac{2}{3} J^2 - \frac{29}{3} J_3^2 + 4[J^2 - J_3^2] J_3^2 \right) + \dots \right\} t \right]. \quad (11)$$

The rotation operator  $R(t)$  is deducible from (4), (6), (7) and

(11), when we employ (2) to write down from (2.35) of ref. 1

$$\varepsilon F^{(1)}(t) = -i \sum_{r=1,2} \int_0^t J_r \omega_r(t_r) dt_r \\ \varepsilon^2 F^{(2)}(t) = \gamma(J^2 - J_3^2)(\beta t - 1 + e^{-\beta t}) - \sum_{r,s=1,2} \int_0^t dt_r \int_0^{t_r} dt_s J_r J_s \omega_r(t_r) \omega_s(t_s) \\ \varepsilon^3 F^{(3)}(t) = i \int_0^t dt_r \int_0^{t_r} dt_s \int_0^{t_s} dt_3 \left\{ \sum_{a,b,c=1,2} J_a J_b J_c \omega_a(t_r) \omega_b(t_s) \omega_c(t_3) \right. \\ \left. - (J^2 - J_3^2) \frac{kT}{I} \left[ \sum_{a=1,2} J_a \omega_a(t_r) e^{-\beta(t_r - t_3)} - \sum_{b=1,2} J_b \omega_b(t_s) e^{-\beta(t_s - t_3)} \right. \right. \\ \left. \left. - \sum_{c=1,2} J_c \omega_c(t_3) e^{-\beta(t_r - t_3)} \right] \right\}. \quad (12)$$

the last term of (2.35) vanishing because  $\omega_i$  is centred and Gaussian, and employ (2.36) of ref. 1 to write down

$$\varepsilon^4 F^{(4)}(t) = - \int_0^t \varepsilon^4 \Omega^{(4)}(t_r) dt_r - i \sum_{a=1,2} \int_0^t J_a \omega_a(t_r) \varepsilon^3 F^{(3)}(t_r) dt_r \\ - \int_0^t \varepsilon^2 F^{(2)}(t_r) \varepsilon^2 \Omega^{(2)}(t_r) dt_r. \quad (13)$$

Let us calculate  $\langle R(t) \omega_\mu(t) \omega_\nu(0) \rangle$ . We see from (4) that, since  $F^{(1)}(t)$  and  $F^{(3)}(t)$  contain only terms with an odd number of  $\omega_i$ 's

$$\langle R(t) \omega_\mu(t) \omega_\nu(0) \rangle = \left( \langle \omega_\mu(t) \omega_\nu(0) \rangle \frac{1}{I} + \langle \varepsilon^2 F^{(2)}(t) \omega_\mu(t) \omega_\nu(0) \rangle \right. \\ \left. + \langle \varepsilon^4 F^{(4)}(t) \omega_\mu(t) \omega_\nu(0) \rangle + \dots \right) \langle R(t) \rangle. \quad (14)$$

From (2) we have

$$\langle \omega_\mu(t) \omega_\nu(0) \rangle \frac{1}{I} = \delta_{\mu\nu} \frac{kT}{I} \frac{1}{I} e^{-\beta t}. \quad (15)$$

The evaluation of  $\langle \varepsilon^2 F^{(2)}(t) \omega_\mu(t) \omega_\nu(0) \rangle$  and  $\langle \varepsilon^4 F^{(4)}(t) \omega_\mu(t) \omega_\nu(0) \rangle$  is performed in much the same way as for a spherical molecule<sup>9)</sup>. It is found without difficulty that

$$\langle \varepsilon^2 F^{(2)}(t) \omega_\mu(t) \omega_\nu(0) \rangle = -\gamma \frac{kT}{I} \left\{ J_\mu J_\nu [1 - 2e^{-\beta t} + e^{-2\beta t}] \right. \\ \left. + i(J_\mu \frac{e_\mu \times e_\nu}{I} - e_\nu \times e_\mu) [-e^{-\beta t} + \beta t e^{-\beta t} + e^{-2\beta t}] \right\}. \quad (16)$$

To calculate  $\langle \varepsilon^4 F^{(4)}(t) \omega_\mu(t) \omega_\nu(0) \rangle$  we employ the following relations derived from (3):

$$\begin{aligned}
\sum_{k,l=1,2} J_k J_l J_k J_l &= (J^2 - J_3^2)^2 - J^2 + 2J_3^2 \\
\sum_{k,l=1,2} J_k J_l J_k J_l &= (J^2 - J_3^2)^2 - J^2 + 3J_3^2 \\
\sum_{k,l=1,2} J_k J_l J_k J_l &= J_k J_l (J^2 - J_3^2 - J^2) - 2i J_k (J_\mu \cdot e_\nu \times e_3) J_3 \\
\sum_{k,l=1,2} J_k J_l J_k J_l &= J_k J_l (J^2 - J_3^2 - J^2) - i J_k (J_\mu \cdot e_\nu \times e_3) J_3 \\
\sum_{k,l=1,2} J_k J_l J_k J_l &= (J^2 - J_3^2 - J^2) J_k J_l + i J_3 (J_\mu \cdot e_\nu \times e_3) J_l \\
\sum_{k,l=1,2} J_k J_l J_k J_l &= (J^2 - J_3^2 - J^2) J_k J_l + i J_3 (J_\mu \cdot e_\nu \times e_3) J_l \\
&+ i (J_\mu \cdot e_\nu \times e_3) J_k J_l.
\end{aligned}$$

We deduce that

$$\begin{aligned}
\langle \xi^4 F^{(4)}(t) \omega_\mu(t) \omega_\nu(t) \rangle &= -\gamma^2 \frac{kT}{I} (J^2 - J_3^2) J_k J_l (1 + \frac{3}{2} e^{-Bt} - 3Bt e^{-Bt} - 3 e^{-2Bt} + \frac{1}{2} e^{-3Bt}) \\
&+ i (J_\mu \cdot e_\nu \times e_3) \left( \frac{1}{2} e^{-Bt} - Bt e^{-Bt} + \frac{1}{2} B^2 t^2 e^{-Bt} - e^{-2Bt} + \frac{1}{2} e^{-3Bt} \right) \\
&+ \left( \frac{kT}{I} \right)^3 \left\{ \left[ -J_k J_l - J_3^2 J_k J_l + J_k J_l J^2 - 2i J_k (J_\mu \cdot e_\nu \times e_3) J_l \right] \int_0^t dt_1 \dots \int_0^{t_3} dt_4 e^{-B(t-t_1-t_2-t_3-t_4)} \right. \\
&+ \left[ -J_k J_l - i J_k (J_\mu \cdot e_\nu \times e_3) J_l \right] \int_0^t dt_1 \dots \int_0^{t_3} dt_4 e^{-B(t-t_1-t_2-t_3-t_4)} \\
&+ \left[ 2J^2 - 2J_3^2 \right] J_k J_l - J_k J_l + i J_k (J_\mu \cdot e_\nu \times e_3) J_l \int_0^t dt_1 \dots \int_0^{t_3} dt_4 e^{-3(t-t_1-t_2-t_3-t_4)} \\
&+ \left[ 2J^2 - 3J_3^2 \right] J_k J_l - J_k J_l + i J_k (J_\mu \cdot e_\nu \times e_3) J_l \int_0^t dt_1 \dots \int_0^{t_3} dt_4 e^{-3(t-t_1-t_2-t_3-t_4)} \\
&+ \left[ 2J^2 - 3J_3^2 \right] J_k J_l - J_k J_l + i J_k (J_\mu \cdot e_\nu \times e_3) J_l \int_0^t dt_1 \dots \int_0^{t_3} dt_4 e^{-3(t-t_1-t_2-t_3-t_4)} \\
&+ \left[ 2J^2 - 3J_3^2 \right] J_k J_l - J_k J_l + i J_k (J_\mu \cdot e_\nu \times e_3) J_l \int_0^t dt_1 \dots \int_0^{t_3} dt_4 e^{-3(t-t_1-t_2-t_3-t_4)} \\
&- 3i J_k (J_\mu \cdot e_\nu \times e_3) J_l \int_0^t dt_1 \dots \int_0^{t_3} dt_4 e^{-3(t-t_1-t_2-t_3-t_4)} \}.
\end{aligned} \quad (17)$$

The value of  $\langle R(t) \omega_\mu(t) \omega_\nu(t) \rangle$  may now be written down from (11), (14) - (17).

### 3. THE LAPLACE TRANSFORM OF $\langle R(t) \omega_\mu(t) \omega_\nu(t) \rangle$

The contributions  $\langle 1/T_1 \rangle$ ,  $\langle 1/T_2 \rangle$ , from the spin-rotational interactions to the reciprocals  $T_1^{-1}$ ,  $T_2^{-1}$  of the longitudinal and transverse relaxation times, respectively, are given by<sup>10)</sup>

$$\left( \frac{1}{T_1} \right) = 2 J_1(\omega_0), \quad \left( \frac{1}{T_2} \right) = J_1(\omega_0) + J_1(\omega_0), \quad (18)$$

where  $\omega_0$  is the angular velocity of the Larmor precession,

$$J_1(\omega) = \frac{1}{2} \left( C_{11}^{00}(\omega) + C_{11}^{00}(\omega) \right) \quad (19)$$

and, for the linear model,

$$C_{11}^{00}(\omega) = \frac{I^2}{3kT} \sum_{\mu,\nu=1,2} \sum_{m,n=-1}^1 (-1)^m R_{\mu,\nu}^i R_{\mu,\nu}^i \left( \int_0^\infty e^{-st} \langle R(t) \omega_\mu(t) \omega_\nu(t) \rangle dt \right)_{n,m} \quad (20)$$

In the last equation we have the  $\eta_{n,m}$  — element of the Laplace transform of  $\langle R(t) \omega_\mu(t) \omega_\nu(t) \rangle$  in the representation with basis  $Y_{l,m}(\beta_{10}, \alpha_{10})$  form of  $\langle R(t) \omega_\mu(t) \omega_\nu(t) \rangle$  in the representation with basis  $Y_{l,m}(\beta_{10}, \alpha_{10})$  angles specifying the orientation of the positive third axis of the rotating system with respect to the laboratory coordinate system. When the  $i$ th nucleus is on the line of symmetry, the  $R^i$ 's are given by

$$R_{1,1}^i = \frac{C_1}{\sqrt{2}}, \quad R_{1,2}^i = \frac{i C_1}{\sqrt{2}}, \quad R_{1,3}^i = 0 \quad (21)$$

$R_{0,1}^i = R_{0,2}^i = 0$ ,  $R_{0,3}^i = C_{11}$ , and so are independent of  $i$ . Since  $\mu, \nu \neq 3$ ,  $C_{11}$  will not now appear in (20) and zero values of  $\eta_{1,1}$  and  $\eta_{1,2}$  will not appear. We may therefore rewrite (20) simply as

$$C(s) = -\frac{I^2}{3\hbar^2} \sum_{\mu, \nu=1,2} \sum_{m, n=\pm 1} b_{n\mu} b_{m\nu} \left( \int_0^\infty e^{-st} \langle R(t) \omega_\mu(t) \omega_\nu(0) \rangle dt \right)_{n, -m} \quad (22)$$

In the extreme narrowing case of  $\omega_0 \ll \hbar T / (IB)^{1/2}$  we may replace  $\omega_0$  in (18) by zero. Then  $(1/T_1)$ , and  $(1/T_2)$ , are equal, and writing  $1/T_{sr}$  for their common value we deduce from (19) that

$$\frac{1}{T_{sr}} = 2C(0). \quad (23)$$

The spin-rotational correlation time  $\tau_{sr}$  for the linear molecule is, from eq. (2.27) of ref. 1 and the above restrictions on  $\mu$  and  $m$ , given by

$$\tau_{sr} = -\frac{3\hbar^2}{kTI} \frac{C(0)}{\sum_{\mu=1,2} \sum_{m=\pm 1} b_{-m\mu} b_{m\mu}}$$

Since

$$\sum_{\mu=1,2} \sum_{m=\pm 1} b_{m\mu} b_{m\mu} = 2 \sum_{\mu=1,2} b_{1\mu} b_{1\mu} = -2C_1^2,$$

by (21),

$$\tau_{sr} = \frac{3\hbar^2 C(0)}{2C_1^2 kTI} \quad (24)$$

In the above-mentioned representation

$$J_1 = \frac{1}{\sqrt{2}} \begin{bmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{bmatrix}, J_2 = \frac{i}{\sqrt{2}} \begin{bmatrix} 0 & -1 & 0 \\ 1 & 0 & -1 \\ 0 & 1 & 0 \end{bmatrix}, J_3 = \begin{bmatrix} -1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix}, \quad (25)$$

with the rows and columns numbered in the order  $-1, 0, 1$ . It follows that

$$J_1^2 = \begin{bmatrix} \frac{1}{2} & 0 & \frac{1}{2} \\ 0 & 1 & 0 \\ \frac{1}{2} & 0 & \frac{1}{2} \end{bmatrix}, J_2^2 = \begin{bmatrix} \frac{1}{2} & 0 & -\frac{1}{2} \\ 0 & 1 & 0 \\ -\frac{1}{2} & 0 & \frac{1}{2} \end{bmatrix}, J_3^2 = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$J_1 J_2 = \frac{i}{\sqrt{2}} \begin{bmatrix} 1 & 0 & -1 \\ 0 & 0 & 0 \\ 1 & 0 & -1 \end{bmatrix}, J_2 J_1 = \frac{i}{\sqrt{2}} \begin{bmatrix} -1 & 0 & 1 \\ 0 & 0 & 0 \\ 1 & 0 & 1 \end{bmatrix}, J_1^2 J_3^2 = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 2 & 0 \\ 0 & 0 & 1 \end{bmatrix}.$$

From (21), (25) and (26) we find that

$$\sum_{\mu, \nu=1,2} \sum_{m, n=\pm 1} b_{n\mu} b_{m\nu} \delta_{\mu\nu} (I)_{n, -m} = \sum_{\mu=1,2} \sum_{m=\pm 1} b_{-m\mu} b_{m\mu} = -2C_1^2, \quad (26)$$

$$\begin{aligned} & \sum_{\mu, \nu=1,2} \sum_{m, n=\pm 1} b_{n\mu} b_{m\nu} i (J_\mu \times J_\nu)_{n, -m} \\ &= i \sum_{m, n=\pm 1} (b_{n1} b_{m2} - b_{n2} b_{m1}) (J_3)_{n, -m} \\ &= i \{ -(b_{-11} b_{12} - b_{-12} b_{11}) + (b_{11} b_{-12} - b_{12} b_{-11}) \} = 2C_1^2, \end{aligned} \quad (27)$$

$$\begin{aligned} & \sum_{\mu, \nu=1,2} b_{n\mu} b_{m\nu} (J_\mu J_\nu)_{n, -m} \\ &= \sum_{m, n=\pm 1} \{ b_{n1} b_{m1} (J_1^2)_{n, -m} + b_{n2} b_{m2} (J_2^2)_{n, -m} + b_{n1} b_{m2} (J_1 J_2)_{n, -m} + b_{n2} b_{m1} (J_2 J_1)_{n, -m} \} \\ &= 0. \end{aligned} \quad (28)$$

Equations (27) - (29) could have been obtained by putting  $C_{11} = D$  in (3.36) - (3.38) of ref. 1.

Since  $\mu$  and  $\nu$  can assume only the values 1, 2, it follows from (25) and (26) that

$$\begin{aligned} J_3^2 (\underline{J} \cdot \underline{e}_\mu \times \underline{e}_\nu) &= (\underline{J} \cdot \underline{e}_\mu \times \underline{e}_\nu) J_3^2 = (\underline{J} \cdot \underline{e}_\mu \times \underline{e}_\nu) \\ J_3^2 J_\mu J_\nu &= J_\mu J_\nu J_3^2. \end{aligned} \quad (30)$$

By employing these relations we may deduce that

$$\begin{aligned} i J_\mu (\underline{J} \cdot \underline{e}_\nu \times \underline{e}_3) J_3 &= -J_\mu J_\nu \\ i J_3 (\underline{J} \cdot \underline{e}_\mu \times \underline{e}_3) J_\nu &= J_\mu J_\nu \end{aligned} \quad (31)$$

$$i (\underline{J} \cdot \underline{e}_\mu \times \underline{e}_3) J_\nu J_3 = -J_\mu J_\nu - i (\underline{J} \cdot \underline{e}_\mu \times \underline{e}_\nu) + \delta_{\mu\nu} \underline{I}.$$

On introducing (30) and (31) into (17) and employing (11), (14) - (16) we

conclude that

$$\begin{aligned} \langle R(t) \omega_\lambda(t) \omega_\nu(0) \rangle &= \left[ \delta_{\mu\nu} \frac{kT}{I} \underline{I} e^{-Bt} \right. \\ &- \gamma \frac{kT}{I} \left\{ J_\mu J_\nu [1 - 2e^{-Bt} + e^{-2Bt}] + i (\underline{J} \cdot \underline{e}_\mu \times \underline{e}_\nu) [-e^{-Bt} + Bte^{-Bt} + e^{-2Bt}] \right\} \\ &- \gamma^2 \frac{kT}{I} (J^2 - J_3^2) \left\{ J_\mu J_\nu (1 + \frac{3}{2} e^{-Bt} - 3Bte^{-Bt} - 3e^{-2Bt} + \frac{1}{2} e^{-3Bt}) \right. \\ &\quad \left. + i (\underline{J} \cdot \underline{e}_\mu \times \underline{e}_\nu) (\frac{1}{2} e^{-3Bt} - Bte^{-Bt} - \frac{1}{2} Bt^2 e^{-Bt} - e^{-2Bt} + Bte^{-2Bt} + \frac{1}{2} e^{-3Bt}) \right\} \\ &+ \left( \frac{kT}{I} \right)^3 \left\{ J_\mu J_\nu \int_0^t dt_1 \dots \int_0^{t_3} dt_4 e^{-B(t-t_1+t_2-t_3+t_4)} \right. \\ &\quad + [4J_\mu J_\nu - 2J_\mu J_\nu J_3^2] \int_0^t dt_1 \dots \int_0^{t_2} dt_4 e^{-B(t+t_1-t_2-t_3+t_4)} \\ &\quad + [\delta_{\mu\nu} \underline{I} + i (\underline{J} \cdot \underline{e}_\mu \times \underline{e}_\nu) + 3J_\mu J_\nu - 2J_\mu J_\nu J_3^2] \int_0^t dt_1 \dots \int_0^{t_3} dt_4 e^{-B(t+t_1-t_2+t_3-t_4)} \\ &\quad \left. + [\delta_{\mu\nu} \underline{I} + 2i (\underline{J} \cdot \underline{e}_\mu \times \underline{e}_\nu) + 4J_\mu J_\nu - 2J_\mu J_\nu J_3^2] \int_0^t dt_1 \dots \int_0^{t_2} dt_4 e^{-B(t+t_1+t_2-t_3-t_4)} \right\} \\ &\times \left[ \underline{I} + \gamma (J^2 - J_3^2) (1 - e^{-Bt}) + \gamma^2 \left\{ (2J^2 - 5J_3^2) \left( \frac{5}{6} - Bte^{-Bt} - e^{-Bt} - \frac{1}{4} e^{-2Bt} \right) \right. \right. \\ &\quad \left. \left. + (J^2 - J_3^2) \left( \frac{1}{2} - e^{-Bt} + \frac{1}{2} e^{-2Bt} \right) \right\} + \dots \right] e^{Gt}, \end{aligned} \quad (32)$$

where

$$G = -\gamma B \left\{ (J^2 - J_3^2) + \gamma (J^2 - \frac{5}{2} J_3^2) + \gamma^2 \left( \frac{8}{3} J^2 - \frac{29}{3} J_3^2 + 4 [J^2 - J_3^2] J_3^2 \right) + \dots \right\}. \quad (33)$$

We see from (26) and (33) that  $G$  is a diagonal matrix with its  $-1, -1$  — and  $1, 1$  — elements equal. The same is true for  $-G + a \underline{I}$  and  $(-G + a \underline{I})^{-1}$ . It follows from this that the quantities  $-G + a \underline{I}$ ,  $-G + b \underline{I}$ ,  $(-G + c \underline{I})^{-1}$ ,  $(-G + f \underline{I})^{-1}$  commute with each other<sup>13)</sup>. In order to study the behaviour of  $e^{Gt}$  as  $t$  becomes indefinitely large we approximate  $G$  in (33) by  $-\gamma B (J^2 - J_3^2)$ , so that

$$G = -\gamma B \underline{I} - \gamma B \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}.$$

Then

$$t^r e^{Gt} = t^r e^{-\gamma Bt} \begin{bmatrix} 0 & 0 & 0 \\ 0 & \exp(-\gamma Bt) & 0 \\ 0 & 0 & 0 \end{bmatrix},$$

and so

$$\lim_{t \rightarrow \infty} (t^r e^{Gt}) = 0. \quad (34)$$

Let us consider  $\int_0^\infty t^2 e^{-bt} e^{Gt} dt$  with  $b \geq 0$ . By expanding the exponential operators as series we readily find that

$$\begin{aligned} \frac{d}{dt} \left\{ -(-G + b \underline{I})^{-1} t^2 \exp[(G - b \underline{I})t] - 2(-G + b \underline{I})^{-2} t \exp[(G - b \underline{I})t] \right. \\ \left. + 2(-G + b \underline{I})^{-3} - 2(-G + b \underline{I})^{-3} \exp[(G - b \underline{I})t] \right\} \\ = t^2 \exp[(G - b \underline{I})t]. \end{aligned}$$

Hence

$$\begin{aligned} \int_0^\infty t^2 e^{-bt} e^{Gt} dt &= \int_0^\infty t^2 \exp[(G - b \underline{I})t] dt \\ &= 2(-G + b \underline{I})^{-3} + \lim_{t \rightarrow \infty} \left\{ -(-G + b \underline{I})^{-1} t^2 e^{-bt} e^{Gt} - 2(-G + b \underline{I})^{-2} t e^{-bt} e^{Gt} \right. \\ &\quad \left. - 2(-G + b \underline{I})^{-3} e^{-bt} e^{Gt} \right\} \\ &= 2(-G + b \underline{I})^{-3}, \end{aligned}$$



on employing (34), and similarly

$$\int_0^t e^{-st} e^{st} dt = \gamma! (-G + B\tilde{I})^{-\gamma-1} \quad (\gamma = 0, 1, 2, 3, \dots) \quad (35)$$

To obtain the Laplace transform of  $\langle R(t) \omega_\mu(t) \omega_\nu(t) \rangle$  as given by (32) and (33), we employ standard methods<sup>14</sup> which in the integration procedure are applicable to the present problem, since there is only one non-commuting quantity multiplying  $\tilde{C}$ . Thus, for example,

$$\begin{aligned} \int_0^\infty e^{-st} dt \int_0^t dt_1 \int_0^{t_1} dt_2 \int_0^{t_2} dt_3 \int_0^{t_3} dt_4 e^{-B(t-t_1-t_2-t_3-t_4)} e^{Gt} \\ = \int_0^\infty e^{-st} dt \int_0^t dt_1 \dots \int_0^{t_3} dt_4 \exp[(G-B\tilde{I})(t-t_1) + G(t_1-t_2) + (G-B\tilde{I})(t_2-t_3) \\ + G(t_3-t_4) + (G-B\tilde{I})t_4] \\ = \int_0^\infty e^{-st} dt \left\{ \exp[(G-B\tilde{I})t] * e^{Gt} * \exp[(G-B\tilde{I})t] * e^{Gt} * \exp[(G-B\tilde{I})t] \right\} \\ = (-G + B\tilde{I})^{-2} (-G + [S+B\tilde{I}])^{-3}. \end{aligned}$$

This result may be verified by putting<sup>15</sup>

$$\int_0^t dt_1 \dots \int_0^{t_3} dt_4 e^{B(t_1-t_2-t_3-t_4)} = B^{-4} (\frac{1}{2} B^2 t^2 + 2Bt + 3 + Bte^{Bt} - 3e^{Bt})$$

and using (35). We then deduce from (32) that up to terms of order  $\gamma^2 kT/\eta B$

$$\begin{aligned} \int_0^\infty e^{-st} \langle R(t) \omega_\mu(t) \omega_\nu(t) \rangle dt \\ = \frac{kT}{I} \delta_{\mu\nu} \left\{ [\tilde{I} + \gamma(J^2 - J_3^2)] + \gamma \left[ \frac{5}{4} (2J^2 - 5J_3^2) + \frac{1}{4} (J^2 - J_3^2) \right] (-G + [S+B\tilde{I}])^{-1} \right. \\ \left. - \gamma (J^2 - J_3^2) (-G + [S+2B\tilde{I}])^{-1} \right. \\ \left. + \gamma^2 \left[ -(2J^2 - 5J_3^2) B (-G + [S+2B\tilde{I}])^{-2} \right. \right. \\ \left. - [(2J^2 - 5J_3^2) + (J^2 - J_3^2)] (-G + [S+2B\tilde{I}])^{-1} \right. \\ \left. + [-\frac{1}{4} (2J^2 - 5J_3^2) + \frac{1}{4} (J^2 - J_3^2)] (-G + [S+3B\tilde{I}])^{-1} \right] \} \\ - \gamma \frac{kT}{I} \left\{ J_{\mu\nu} [\tilde{I} + \gamma(J^2 - J_3^2)] + \gamma \left[ \frac{5}{4} (2J^2 - 5J_3^2) + \frac{1}{4} (J^2 - J_3^2) \right] (-G + S\tilde{I})^{-1} \right. \\ \left. + J_{\mu\nu} [-2(-G + [S+B\tilde{I}])^{-1} + (-G + [S+2B\tilde{I}])^{-1}] \right. \\ \left. + \gamma J_{\mu\nu} (J^2 - J_3^2) [-2(-G + [S+B\tilde{I}])^{-1} + 3(-G + [S+2B\tilde{I}])^{-1} - (-G + [S+3B\tilde{I}])^{-1}] \right. \\ \left. + i(J_{\mu\nu} \cdot \underline{e}_\mu \times \underline{e}_\nu) [-(-G + [S+B\tilde{I}])^{-1} + B(-G + [S+2B\tilde{I}])^{-1} + (-G + [S+3B\tilde{I}])^{-1}] \right. \\ \left. + \gamma i(J_{\mu\nu} \cdot \underline{e}_\mu \times \underline{e}_\nu) [-(-G + [S+B\tilde{I}])^{-1} + B(-G + [S+2B\tilde{I}])^{-1} + 2(-G + [S+3B\tilde{I}])^{-1}] \right. \\ \left. - B(-G + [S+2B\tilde{I}])^{-2} - (-G + [S+3B\tilde{I}])^{-1} \right] \\ - \gamma \frac{kT}{I} \frac{1}{I} \left\{ J_{\mu\nu} J_{\nu\lambda} \left\{ J_{\lambda\mu} [\tilde{I} + \gamma(J^2 - J_3^2)] + \gamma \left[ \frac{5}{4} (2J^2 - 5J_3^2) + \frac{1}{4} (J^2 - J_3^2) \right] (-G + [S+B\tilde{I}])^{-1} \right. \right. \\ \left. \left. - 3(-G + [S+2B\tilde{I}])^{-1} + \frac{1}{2} (-G + [S+3B\tilde{I}])^{-1} \right] \right. \\ \left. + i(J_{\mu\nu} \cdot \underline{e}_\mu \times \underline{e}_\nu) \left[ \frac{1}{2} (-G + [S+B\tilde{I}])^{-1} - B(-G + [S+2B\tilde{I}])^{-1} + B(-G + [S+3B\tilde{I}])^{-1} \right. \right. \\ \left. \left. - (-G + [S+2B\tilde{I}])^{-1} + B(-G + [S+3B\tilde{I}])^{-1} \right] + \frac{1}{2} (-G + [S+3B\tilde{I}])^{-1} \right\} \\ + \left( \frac{kT}{I} \right)^2 \left\{ J_{\mu\nu} J_{\nu\lambda} \left\{ J_{\lambda\mu} [\tilde{I} + \gamma(J^2 - J_3^2)] + \gamma \left[ \frac{5}{4} (2J^2 - 5J_3^2) + \frac{1}{4} (J^2 - J_3^2) \right] (-G + S\tilde{I})^{-1} \right. \right. \\ \left. \left. + [4J_{\mu\nu} J_{\nu\lambda} - 2J_{\mu\nu} J_{\nu\lambda} J_{\lambda\mu}] [\tilde{I} + \gamma(J^2 - J_3^2)] (-G + S\tilde{I})^{-1} - (-G + [S+2B\tilde{I}])^{-1} - (-G + [S+3B\tilde{I}])^{-1} \right. \right. \\ \left. \left. + [S_{\mu\nu} \tilde{I} + i(\tilde{I} \cdot \underline{e}_\mu \times \underline{e}_\nu) + 3\tilde{I} \cdot \underline{e}_\mu \times \underline{e}_\nu] (-G + [S+B\tilde{I}])^{-1} - (-G + [S+2B\tilde{I}])^{-1} - (-G + [S+3B\tilde{I}])^{-1} \right. \right. \\ \left. \left. + [S_{\mu\nu} \tilde{I} + 2i(\tilde{I} \cdot \underline{e}_\mu \times \underline{e}_\nu) + 4\tilde{I} \cdot \underline{e}_\mu \times \underline{e}_\nu - 2\tilde{I} \cdot \underline{e}_\mu \underline{e}_\nu] (-G + S\tilde{I})^{-1} - (-G + [S+B\tilde{I}])^{-1} \right. \right. \\ \left. \left. \times (-G + [S+2B\tilde{I}])^{-1} - (-G + [S+3B\tilde{I}])^{-1} \right\} \right\}. \end{aligned}$$

## 4. CALCULATION OF RELAXATION TIMES

We return to eq. (22),

$$C(s) = -\frac{I^2}{3k^2} \sum_{\mu, \nu=1,2} \sum_{m, n=\pm 1} b_{m\mu} b_{n\nu} \left( \int_0^\infty e^{-st} \langle R(t) \omega_\mu(t) \omega_\nu(0) \rangle dt \right)_{n, -m}$$

Since we have no contributions for  $m=0$  or  $n=0$ ,  $J_3^2$  in the computation of  $C(s)$  behaves like the unit matrix. The same is true of  $G$ , as given by (9), and therefore of  $(-G + bI)^{-1}$ . Hence  $J_\mu J_\nu$  multiplied into products of  $J_3^2$  and operators of the type  $(-G + bI)^{-1}$  is a constant times  $J_\mu J_\nu$ . By (29), all such products give zero contribution to  $C(s)$ . We may therefore ignore all terms involving  $J_\mu J_\nu$  that occur in (36).

In order to simplify the calculations we shall put  $s$  equal to zero and denote by  $C_1(0)$  the value of  $C(0)$  with the  $J_\mu J_\nu$  -terms omitted. Then from (23) and (24)

$$\frac{1}{T_{sr}} = 2C_1(0), \quad \tau_{sr} = \frac{3k^2 C_1(0)}{2C_1^2 kT I} \quad (37)$$

From (22) and (36)

$$\begin{aligned} C_1(0) = & -\frac{I^2}{3k^2} \sum_{\mu, \nu=1,2} \sum_{m, n=\pm 1} b_{m\mu} b_{n\nu} \\ & \times \left[ \frac{kT}{I} \delta_{\mu\nu} \left\{ [I + \gamma(J^2 - J_3^2) + \gamma^2 \left[ \frac{1}{4}(2J^2 - 5J_3^2) + \frac{1}{2}(J^2 - J_3^2)^2 \right]] (-G + BI)^{-1} \right. \right. \\ & \quad \left. \left. - \gamma(J^2 - J_3^2)(-G + 2BI)^{-1} \right. \right. \\ & \quad \left. \left. + \gamma^2 \left[ -(2J^2 - 5J_3^2)B(-G + 2BI)^{-1} \left[ (2J^2 - 5J_3^2) + (J^2 - J_3^2)^2 \right] (-G + 2BI)^{-1} \right. \right. \right. \right. \\ & \quad \left. \left. \left. + \left[ -\frac{1}{4}(2J^2 - 5J_3^2) + \frac{1}{2}(J^2 - J_3^2)^2 \right] (-G + 3BI)^{-1} \right] \right\} \right. \\ & \quad \left. - \gamma \frac{kT}{I} i(J_\mu \cdot e_\mu \times e_\nu) \left\{ -(1+\gamma)(-G + BI)^{-1} + (1+\gamma)B(-G + BI)^{-1} \right. \right. \\ & \quad \left. \left. + (1+2\gamma)(-G + 2BI)^{-1} - \gamma B(-G + 2BI)^{-1} - \gamma(-G + 3BI)^{-1} \right\} \right. \\ & \quad \left. - \gamma^2 \frac{kT}{I} i(J_\mu \cdot e_\mu \times e_\nu) \left\{ \frac{1}{2}(-G + BI)^{-1} - B(-G + BI)^{-1} + B^2(-G + BI)^{-1} \right. \right. \\ & \quad \left. \left. - (-G + 2BI)^{-1} + B(-G + 2BI)^{-1} + \frac{1}{2}(-G + 3BI)^{-1} \right\} \right. \\ & \quad \left. + \left( \frac{kT}{I} \right)^3 \left\{ [\delta_{\mu\nu} I + i(J_\mu \cdot e_\mu \times e_\nu)] (-G + BI)^{-1} (-G + 2BI)^{-1} \right. \right. \\ & \quad \left. \left. + [\delta_{\mu\nu} I + 2i(J_\mu \cdot e_\mu \times e_\nu)] (-G + BI)^{-1} (-G + 2BI)^{-1} (-G + 3BI)^{-1} \right\} \right] \quad (38) \end{aligned}$$

In the representation (25) eq. (9) gives

$$G = -\gamma B \begin{bmatrix} 1 - \frac{1}{2}\gamma - \frac{1}{3}\gamma^2 + \dots & 0 & 0 \\ 0 & 2 + 2\gamma + \frac{16}{3}\gamma^2 + \dots & 0 \\ 0 & 0 & 1 - \frac{1}{2}\gamma - \frac{1}{3}\gamma^2 + \dots \end{bmatrix}$$

It follows that

$$(-G + BI)^{-1} = \frac{1}{B} \begin{bmatrix} 1 - \gamma + \frac{3}{2}\gamma^2 + \dots & 0 & 0 \\ 0 & 1 - 2\gamma + 2\gamma^2 + \dots & 0 \\ 0 & 0 & 1 - \gamma + \frac{3}{2}\gamma^2 + \dots \end{bmatrix} \quad (39)$$

which may be replaced by  $(1 - \gamma + \frac{3}{2}\gamma^2 + \dots)B^{-1}I$  when calculating  $C_1(0)$ .

Similar results are true for  $(-G + 2BI)^{-1}$ ,  $(-G + 3BI)^{-1}$ .

Moreover, since we have taken the approximation of the Laplace transform to terms of order  $\gamma^2 kT/(IB)$ , we may put  $G=0$  in the terms of (38) that are proportional to  $\gamma^2(kT/I)$  or  $(kT/I)^3$ .

We find from (38) that the terms in the Laplace transform with  $s=0$  arising from the  $\langle \omega_\mu(t) \omega_\nu(0) \rangle I$  part of  $\langle R(t) \omega_\mu(t) \omega_\nu(0) \rangle$  add up to

$$\frac{kT}{IB} \delta_{\mu\nu} \begin{bmatrix} 1 - \frac{1}{2}\gamma + \frac{1}{2}\gamma^2 + \dots & 0 & 0 \\ 0 & 1 - \gamma + \frac{4}{3}\gamma^2 + \dots & 0 \\ 0 & 0 & 1 - \frac{1}{2}\gamma + \frac{1}{2}\gamma^2 + \dots \end{bmatrix}$$

The contribution  $C_{1a}(0)$  of this to  $C_1(0)$  is given by

$$C_{1a}(0) = -\frac{I^2}{3k^2} \frac{kT}{IB} (1 - \frac{1}{2}\gamma + \frac{1}{2}\gamma^2 + \dots) \sum_{\mu, \nu=1,2} \sum_{m, n=\pm 1} b_{m\mu} b_{n\nu} \delta_{\mu\nu} (I)_{n, -m},$$

so that, by (27),

$$C_{1a}(0) = \frac{2kT I C_1^2}{3k^2 B} (1 - \frac{1}{2}\gamma + \frac{1}{2}\gamma^2 + \dots) \quad (40)$$

Similarly the contribution  $C_{\mu}(0)$  from the  $\langle \varepsilon^2 F^{(2)}(t) \omega_{\mu}(t) \omega_{\mu}(0) \rangle$  part is given by

$$C_{\mu}(0) = -\frac{I^2}{3\pi^2} \frac{kT}{IB} \left( -\frac{1}{2}\gamma + \frac{5}{6}\gamma^2 + \dots \right) \sum_{A,V=1,2} \sum_{m_1, m_2=1}^{\infty} b_{m_1 m_2} i(\vec{J} \cdot \vec{e}_A \times \vec{e}_B)_{m_1 m_2} \quad (41)$$

$$= \frac{2kTIC_1^2}{3\pi^2 B} \left( \frac{1}{2}\gamma - \frac{5}{6}\gamma^2 + \dots \right)$$

on employing (28), and the contribution  $C_{\mu}(0)$  from the  $\langle \varepsilon^4 F^{(4)}(t) \omega_{\mu}(t) \omega_{\mu}(0) \rangle$  part is given by

$$C_{\mu}(0) = \frac{2kTIC_1^2}{3\pi^2 B} \frac{1}{3}\gamma^2 \quad (42)$$

On summing  $C_{\mu}(0)$ ,  $C_{\mu}(0)$ ,  $C_{\mu}(0)$  from (40) - (42) we deduce that

$$C_1(0) = \frac{2kTIC_1^2}{3\pi^2 B}$$

We immediately deduce from (37) that

$$\frac{1}{T_{sr}} = \frac{4kTIC_1^2}{3\pi^2 B} \quad (43)$$

and that

$$\tau_{sr} = \frac{1}{B} \quad (44)$$

If we introduce the friction time  $\tau_F$  defined as in the Debye theory by

$$\tau_F = B^{-1}, \text{ we may express (43) and (44) as}$$

$$\frac{1}{T_{sr}} = \frac{4kTIC_1^2}{3\pi^2} \frac{\tau_F}{B} \quad (45)$$

$$\tau_{sr} = \tau_F \quad (46)$$

Thus to order  $\gamma^2$  the values of  $T_{sr}$  and  $\tau_{sr}$  are independent of  $\gamma$ . This is quite different from what occurs in the case of a spherical molecule, where there are corrections of order  $\gamma^2$ .

# 5. COMPARISON WITH RESULTS FOR THE SYMMETRIC MOLECULE

The value of  $T_{sr}$  for a symmetric top molecule has been expressed by<sup>17)</sup>

$$\frac{1}{T_{sr}} = \frac{2kT}{3\pi^2} \left\{ \frac{2I_1 C_1^2}{B_1 + D_1 + D_3} + \frac{I_3 C_1^2}{B_3 + 2D_1} \right. \quad (4)$$

$$\left. + kT \left[ \left( \frac{2}{B_1^3} + \frac{2I_1}{I_3 B_1^2 B_3} - \frac{2I_3}{I_1 B_1^2 (B_1 + B_3)} \right) C_1^2 \right. \right.$$

$$\left. \left. + \frac{2I_3 (C_1^2 + 2C_1 C_1)}{I_1 B_1 B_3 (B_1 + B_3)} \right] \right\}.$$

Coordinate axes fixed in the body have been taken through the centre of mass, the third axis being along the axis of symmetry.  $I_1$  is the moment of inertia of the body about the first or second coordinate axis and  $I_3$  is that about the third axis, the corresponding frictional constants being  $B_1, B_3$ . The calculations are taken to first order in  $\gamma$  and it is thus allowable to write

$$D_1 = \frac{kT}{I_1 B_1}, \quad D_3 = \frac{kT}{I_3 B_3} \quad (4)$$

We shall attempt to define a limiting process that will enable us to deduce from (47) a result that is consistent with (45). A similar problem was solved in the theory of dielectrics<sup>18)</sup>, where it was found that one could go from the equation for complex permittivity as a function of angular frequency in the case of a symmetric molecule to that for a linear molecule by taking the limits  $I_3 \ll I_1, B_3 \gg B_1$  in such a way that  $I_3 B_3 \gg I_1 B_1$ .

Let us examine the consequences of this limiting process in the present problem. Considering the terms

$$\frac{2I_1 C_1^2}{B_1 + D_1 + D_3}, \quad \frac{I_3 C_{II}^2}{B_3 + 2D_3}$$

in (47) we see that the ratio of the coefficient of  $C_{II}^2$  to the coefficient of  $C_1^2$  is of order  $I_3 B_1 / (I_1 B_3) \ll 1$ , so that we can neglect the  $C_{II}^2$ -terms. Secondly, in the next two lines of (47) we compare the coefficient

$$P \equiv \frac{2I_3}{I_1 B_1 B_3 (B_1 + B_3)},$$

with the coefficient of  $C_1^2$ ,

$$Q = \frac{2}{B_1^3} + \frac{2I_1}{I_3 B_1^2 B_3} - \frac{2I_3}{I_1 B_1^2 (B_1 + B_3)} \\ \div \frac{2I_1 I_3 B_3^2 - 2I_3^2 B_1 B_3}{I_1 I_3 B_1^3 B_3 (B_1 + B_3)} \div \frac{2B_3}{B_1^3 (B_1 + B_3)}.$$

Thus

$$\frac{P}{Q} \div \frac{I_3 B_1^2}{I_1 B_3^2} \ll 1,$$

which shows that the  $(C_{II}^2 + 2C_1 C_{II})$ -term may be neglected in comparison with the  $C_1^2$ -term.

We are therefore left in (47) with

$$\frac{1}{T_{sr}} = \frac{4kT C_1^2}{3\hbar^2} \left\{ \frac{I_1}{B_1 + D_1 + D_3} + \frac{kT B_3}{B_1^3 (B_1 + B_3)} \right\}, \quad (49)$$

Since, from (8) and (48),

$$\frac{D_1}{B_1} = \gamma, \quad \frac{D_3}{B_1} = \frac{I_1 B_1}{I_3 B_3} \ll 1,$$

we may approximate (49) by

$$\frac{1}{T_{sr}} = \frac{4kT I_1 C_1^2}{3\hbar^2 B_1} \left\{ \frac{1}{1+\gamma} + \frac{\gamma}{1+\frac{B_1}{B_3}} \right\} \\ = \frac{4kT I_1 C_1^2}{3\hbar^2 B_1} \{ 1 - \gamma + \gamma (1 - \frac{B_1}{B_3}) + \dots \}.$$

This shows that

$$\frac{1}{T_{sr}} = \frac{4kT I_1 C_1^2}{3\hbar^2 B_1} \{ 1 + o(\gamma) \}$$

and therefore that

$$T_{sr} = T_F \{ 1 + o(\gamma) \}.$$

These confirm (45) and (46).

## o. CONCLUSION

We have shown for the linear molecule that the method proposed for the calculation of the spin-rotational correlation time and of the spin-rotational contributions to the longitudinal and transverse nuclear magnetic relaxation times provides a means of finding these quantities correct to relative order  $(kT/(IB^2))^2$ . This is the order to which we can obtain the same quantities for the spherical model of the molecule. However, the corrections to the zero order expression vanish for the linear molecule. This result may be confirmed to order  $kT/(IB^2)$  by considering a limiting case of a symmetric rotating molecule.

## REFERENCES

- 1) J. McConnell, Dublin Institute for Advanced Studies preprint (1981), DIAS-STP-81-16.
- 2) J. McConnell, Dublin Institute for Advanced Studies preprint (1981), DIAS-STP-81-22.
- 3) ref. 1, eq. (2.33).
- 4) ref. 1, eq. (2.34).
- 5) J. McConnell, Proc. R. Ir. Acad. 78 A (1978), 87.
- 6) J. McConnell, Rotational Brownian Motion and Dielectric Theory (Academic Press, London, New York, Toronto, Sydney, San Francisco, 1980), Appendix D.
- 7) N. M. Krylov and N. N. Bogoliubov, Introduction to Nonlinear Mechanics (Princeton Univ. Press, Princeton, 1947).
- 8) ref. 6, pp. 191, 199.
- 9) ref. 1, subsection 3.1.
- 10) ref. 1, subsection 2.1.
- 11) ref. 1, eq. (3.31).
- 12) A. Abragam, Nuclear Magnetism (Clarendon Press, Oxford, 1961), p.279.
- 13) cf. ref. 6, eq. (12, 5.14).
- 14) ref. 6, Appendix C.
- 15) cf. ref. 6, Appendix D.
- 16) ref. 1, eq. (3.40), (3.43).
- 17) ref. 2, eq. (31).
- 18) J. McConnell, Physica 105 A (1981), 593.